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Anomalous Compressibility of *N*-Isopropylacrylamide Gels near the Volume Phase Transition Temperature

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ABSTRACT: The effect of hydrostatic pressure up to 105.2 MPa on the phase diagram (temperature vs ratio of volume) of *N*-isopropylacrylamide gel and its compressibility near the volume phase transition temperature were examined. The volume phase transition changed from a slightly discontinuous one to a continuous one with increasing pressure, and there seemed to be little change of the transition temperature. The compressibility drastically changed from positive values (swollen phase) to negative values (shrunken phase) at the transition temperature. The volume of the gel for the shrunken phase increased in spite of applying pressure in the vicinity of the transition temperature. The obtained anomalous compressibility was analyzed according to the theory of free energy of the gel.

Introduction

Recently, there has been interest in the volume phase transition of constrained gels from both the theoretical and experimental[1-3] viewpoints because elastic anisotropy affects the character of the phase transition. Hirotsu and Onuki[2] reported that the volume phase transition temperature of *N*-isopropylacrylamide–water gel (NIPA gel) increased upon application of a small stress. Hirotsu[3] also showed that the bulk modulus of the gel became softening and that the Poisson ratio was negative in the vicinity of the transition temperature.

From these results, Li and Tanaka[4] argued that their applied stress had been too small to create any appreciable dispersion in the transition temperature. As known from these investigations, the mechanical properties associated with the volume phase transition of gels are not sufficiently understood. Though there have been many studies of the phase transition, as far as we know, they have been done under atmospheric pressure.

We carried out high-pressure experiments on NIPA gel. Phase diagrams of temperature vs volume ratio (swelling curve) for different hydrostatic pressures and the compressibility near the phase transition temperature were obtained. We analyzed the obtained compressibility according to the theory of the free energy of the gel.

Experimental Section

Preparation of Gel. The sample gels were prepared by a method similar to that described in refs 5 and 6. Monomers of NIPA (main chains) (3.30 g, Kodak) and *N,N*′-methylenebisacrylamide (cross-linker) (55.4 mg, Wako Chemicals) were dissolved in distilled water. The amount of the solution was 41.7 mL. After O_2 gas in the solution was removed by bubbling with N_2 gas, ammonium peroxodisulfate (16.7 mg, Wako Chemicals) and *N,N,N*′,*N*′-tetramethylenediamine (100 μL, Wako Chemicals) were added to the solution as initiators for the polymerization reaction. The ratios of these constituent agents dissolved in the solution were the same as those in ref 5. The solution was transferred into glass tubes of 1-mm diameter. After 24 h at 20 °C, the gels were taken out of the tubes. They were washed in distilled water and cut into ~15-mm strips.

High-Pressure Cell. The high-pressure cell used in the present experiment is shown in Figure 1. It was constructed of SUS 316 stainless steel and designed for pressures up to 200 MPa. The main high-pressure vessel body A of 10.0 × 10.0 × 11.5 cm³ had an axial hole of 2.0-cm diameter, where piston B was fitted in, and four optical windows in 90° geometry. The piston was fixed to the upper plate C. The saphire windows D, 1.5 cm in diameter and 1.0 cm in thickness, were placed in the Teflon window holders. To locate them, we used four rings E, a Viton O-ring, brass and Teflon rings, and a delta ring. Sealing was by these rings. To compress the cell, force was applied to the lower plate F, which supported the main pressure vessel body, from the underside as shown by arrows G. The maximum volume which could be compressed was 20 mL. The pressure was controlled to an accuracy of ±0.5 MPa through the experiment

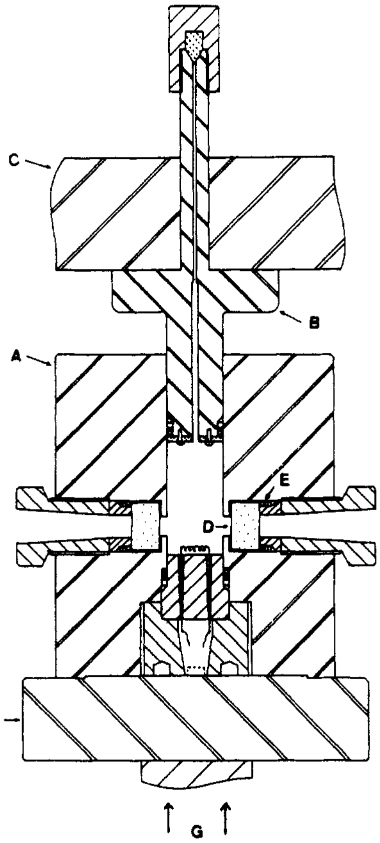

Figure 1. High-pressure cell: (A) main high-pressure vessel body; (B) piston; (C) upper plate for fixing piston: (D) saphire window; (E) Viton, brass, Teflon, and delta rings; (F) lower plate for support of main vessel body; (G) direction of applied force.

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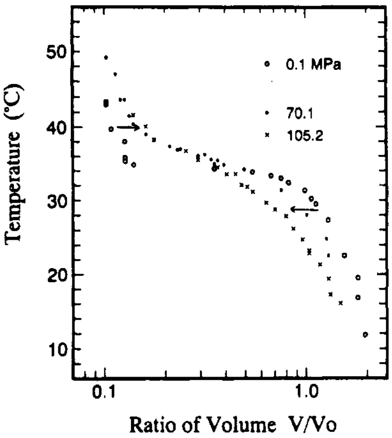

Figure 2. Swelling curves of NIPA gel for three hydrostatic pressures (0.1, 70.1, and 105.2 MPa). Arrows represent the direction of volume change when the gel is compressed at constant temperatures.

and was measured by a Bourdon pressure gauge (Heise). The temperature of the sample was controlled to an accuracy of ±0.1 °C by adjusting the temperature of the water circulating around the main pressure vessel body. A sample gel was put on a glass plate placed at the bottom of the hole. The hole was filled with distilled water, and the water was compressed by the piston. The diameter of the gel was measured with a microscope through the window. Assuming an isotropic nature of the gel, the ratio of the measured diameter D/D_0 was changed to V/V_0 by using the relation $(D/D_0)^3 = V/V_0$. Here, D_0 and V_0 are the diameter and the volume of gel when it was prepared.

Results and Discussion

Figure 2 shows the variation of the swelling curve with increasing pressure (0.1, 70.1, and 105.2 MPa). The swelling curve for 0.1 MPa is very similar to that reported previously.[5,7] A clear and slightly discontinuous transition occurs at 34.5 °C. With increasing pressure, the gel undergoes a continuous crossover, and there seems to be little change of the transition temperature. It is seen that the swelling curves show an unexpected pressure dependence in the vicinity of the phase transition temperature. As shown with arrows, the obtained results mean that if pressure increases at a constant temperature, the volume of gel for the swollen phase will decrease, as expected; on the contrary, however, the volume of gel for the shrunken phase will increase. The latter fact implies the compressibility of the shrunken gel will be negative in the vicinity of the volume phase transition temperature. The pressure dependence of the swelling curve will be discussed elsewhere in more detail. In the present study, we focus our attention on this anomalous compressibility near the phase transition temperature. Thus, we measured the diameter of the gel as a function of pressure at several constant temperatures above and below the transition temperature. The measurements of the diameter were made after the pressure had been kept constant for 24 h because the equilibration time was estimated to be several hours.

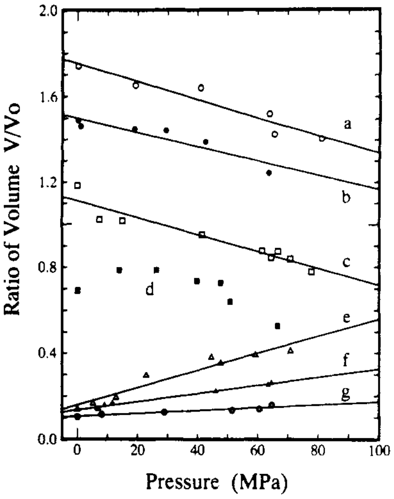

Figure 3. Ratio of volume vs pressure of NIPA gel at constant temperatures: (a) 19.7, (b) 25.9, (c) 30.0, (d) 33.8, (e) 35.8, (f) 37.3, and (g) 39.6 °C. Volume is regarded to be linear to pressure (solid lines).

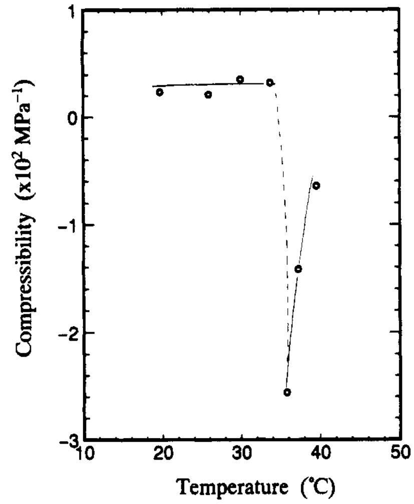

Figure 4. Compressibility of NIPA gel as a function of temperature. Lines are guides for the eye.

Figure 3 shows the obtained pressure dependence of the volume ratio. As expected from the pressure dependence of the swelling curve, the volume of the swollen gel (below the transition temperature) decreases with increasing pressure; however, the volume of the shrunken gel (above the transition temperature) increases in spite of increasing pressure. Though the data points scatter, the volume is regarded to be linear to pressure (solid lines). The compressibility K_T is calculated from the slope of the line by the relation

$$K_T = -1/V(\partial V/\partial P)_T \tag{1}$$

Figure 4 shows the calculated compressibilities as a function of temperature. The compressibility of the swollen gel is approximately 10 times as large as that of water. This implies that the rigidity of water in the gel does not contribute to that of the gel. We suppose the water easily goes out of the gel network when it is compressed. On the contrary, the compressibility of the shrunken gel is negative in the vicinity of the phase transition temperature.

From thermodynamic stability, the compressibility of a material must be positive.[8] From this point of view, the obtained result is very anomalous. Here, we emphasize that the system treated now is not a closed system. In the process of the swelling and the shrinking of the gel, water molecules come into and go out of the gel.

Thus, we think the gel is not such a system as assumed by the above thermodynamic theory. Previously, Hirotsu[3] measured the change of the size of a NIPA gel induced by an applied stress as a function of temperature. He reported that the Poisson ratio of the gel was negative and that the bulk modulus became softening in the vicinity of the volume phase transition temperature. Our result also shows a similar elastic anomaly at the transition temper-

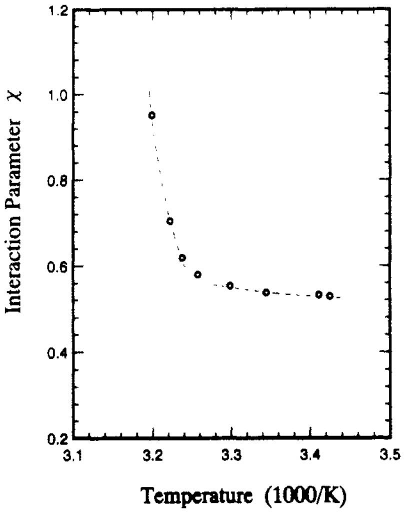

Figure 5. Polymer–solvent interaction parameter χ vs inverse absolute temperature of NIPA gel. Curves are guides for the eye.

ature, but the compressibility exhibits a drastic change to negative values. This behavior differs much from Hirotsu's result showing the softening of the bulk modulus at the transition temperature. We cannot discuss this difference in detail because our stress applied to the gel was much larger than his. As far as we know, such an anomalous compressibility has not been found in other materials.

We will try to analyze the obtained results on the basis of the free energy of the gel. The free energy difference ΔF of a non-ionized gel consists of the mixing free energy of the solvent and polymer and the elastic free energy of the network. It is expressed as[9]

$$\Delta F = k_B T N_s[\ln(1-\phi) + \chi\phi] + (3k_B T N_c/2)[(\phi/\phi_0)^{-2/3} + (1/3)\ln(\phi/\phi_0) - 1] \quad (2)$$

Here, k_B is the Boltzmann constant, N_s and N_c are the number of solvent molecules and the number of polymer chains in the gel, respectively, χ is the polymer–solvent interaction parameter, and T is the absolute temperature. ϕ and ϕ_0 are the volume fraction of the network at T and that when the gel was prepared, respectively. We also use the relation $\phi/\phi_0 = V_0/V$. The inverse of the isothermal compressibility is given by

$$1/K_T = V(\partial^2 \Delta F/\partial V^2)_T \quad (3)$$

Using the above relations, we get

$$1/(k_B T K_T) = (N_A/v_1)[\phi^2/(1-\phi) - 2\chi\phi^2] - (N_c/V_0)[(1/3)(\phi/\phi_0)^{1/3} - (1/2)(\phi/\phi_0)] \quad (4)$$

Here, N_A is Avogadro's number and v_1 is the molar volume of solvent. Using the values of K_T shown in Figure 4 and eq 4, we can estimate χ for various temperatures including the negative compressibility region.

Figure 5 shows the estimated χ as a function of inverse absolute temperature. Here, we used the molecular parameters $v_1 = 18.1$ cm^3, $\phi_0 = 0.075$, and $N_c/V_0 = 1.0 \times 10^{19}$ cm^{-3}. These can be estimated from the initial condition of the preparation of the gel.[5] It is seen that χ depends on temperature and abruptly increases at the transition temperature. This result is very similar to that obtained from the measurement of swelling curves,[5] except that χ changes not discontinuously but continuously at the transition temperature and that the values for the swollen phase are a little larger than 0.5. It has been reported that the phase transition in the gel may occur in a poor solvent. The collapse of the network takes place when $\chi > 0.5$.[10,11] This expectation corresponds to the abrupt increase of χ for the shrunken phase. We also expect that χ should be less than 0.5 for the swollen phase. We cannot clearly explain this discrepancy between the obtained values and this expectation. Here, we only point out that there are the uncertainty and considerable errors in the obtained χ and that we need to take account of the effect of pressure on χ. As clear in eq 4, the estimation of χ depends on the values of the molecular parameters used. But, for example, the real value of N_c/V_0 appropriate for the present gel is not known exactly. We can only use the estimated value. As seen in Figure 3, the data points are scattered for the swollen phase. This causes large errors in the calculation of K_T, that is, χ. Furthermore, we can suppose the obtained values of χ are the mean values in the measured pressure region. As already shown, the phase diagram of the gel changed with pressure. This implies χ changes with pressure. Thus, it is supposed that the obtained values are affected by pressure. We believe that more detailed investigations of the pressure effect on the volume phase transition are needed.

Conclusion

The phase diagram of the NIPA gel was measured for three pressures up to 100 MPa. It was found that the volume phase transition changed from a slightly discontinuous one to a continuous one with increasing pressure, but there seemed to be little change in the transition temperature. We also measured the change of diameter (volume) of the gel as a function of pressure at several constant temperatures. It was found that the volume of the swollen gel decreased with increasing pressure; however, the volume of the shrunken gel increased in the vicinity of the phase transition temperature in spite of applying pressure. The compressibility of NIPA gel drastically changed from positive to negative at the phase transition temperature. We analyzed the obtained compressibility according to the theory of the free energy of the gel and obtained the polymer–solvent interaction parameter χ as a function of temperature. It is found that the obtained χ underwent the abrupt increase at the volume phase transition temperature.

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